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Synthesis, structure, and stereochemistry of 2-alky--4,4,5-trimethyl- and 2-alkyl-4,4,6,6-tetramethyl-1,3-dioxanium perchlorates

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Abstract

A number of 2-alkyl-4,4,5-trimethyl- and 2-alkyl-4,4,6,6-tetramethyl-1,3-dioxanium perchlorates were obtained by acylation of 1,3-diols in the presence of 70% perchloric acid. Acid-catalytic cleavage of the heteroring with subsequent cyclization to 2-alkyl-1,3-dioxanium perchlorates occur in the reaction of 2-aryl(alkyl)-substituted and 2-unsubstituted 1,3-dioxanes with carboxylic acid anhydrides and 70% HClO4. Hypothetical detachment of a hydride ion by means of the acceptor acylium cation does not occur under the investigated conditions. The structures of the synthesized perchlorates were studied by PMR spectroscopy and it was shown that 1,3-dioxanium cations at room temperature exist in a state of rapid conformational isomerization of the "chair-chair" form. The rate of interconversion of the 2,4,4-trimethyl-1,3-dioxanium cation decreases appreciably as the temperature is reduced to -90°. as evidenced by marked broadening of the lines of the protons of the gemdimethyl groupings. © 1977 Plenum Publishing Corporation.

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